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RADIATION INDUCED DEGRADATION OF WHITE THERMAL CONTROL PAINT

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ABSTRACT

This paper details a comparison analysis of the zinc-oxide pigmented white thermal control paints Z-93 and Z-93P. Both paints were simultaneously exposed to combined space environmental effects and analyzed using an in-vacuo reflectance technique. The dose applied to the paints was approximately equivalent to 5 yr in a geosynchronous orbit. This comparison analysis showed that Z-93P is an acceptable substitute for Z-93. Irradiated samples of Z-93 and Z-93P were subjected to additional exposures of ultraviolet (UV) radiation and analyzed using the in-vacuo reflectance technique to investigate UV activated reflectance recovery. Both samples showed minimal UV activated reflectance recovery after an additional 190 equivalent Sun hour (ESH) exposure. Reflectance response utilizing nitrogen as a repressurizing gas instead of air was also investigated. This investigation found the rates of reflectance recovery when repressurized with nitrogen are slower than when repressurized with air.

INTRODUCTION

The Marshall Space Flight Center (MSFC) Space Environmental Effects Branch conducted a series of space environmental effects exposure tests to requalify a new potassium silicate binder used in the production of white thermal control paints Z-93 and YB-71. This requalification program was a joint effort between MSFC, the Air Force Space and Missile System Center, The Aerospace Corporation, NASA's Lewis Research Center, Wright Laboratory, and several other Government and industry facilities.

Z-93 was originally flight qualified with a potassium silicate binder (PS7) from Sylvania. Sylvania discontinued production of PS7 and a new vendor, PQ Corporation, was located to provide the potassium silicate binder denoted as K2130 (ref. 1). The Air Force sponsored and funded this effort at the Illinois Institute of Technology Research Institute (IITRI), and The Aerospace Corporation was the technical lead of this program to requalify three paints, Z-93, YB-71, and S13G/LO-1. The paints using the potassium silicate binder PS7 are denoted as Z-93 and YB-71, while the paints using the K2130 binder are denoted as Z-93P and YB-71P. The S13G/LO-1 paint utilizes a room-temperature vulcanized, silicone, binder. Testing on this paint was not performed at MSFC.

The task performed by the MSFC Space Environmental Effects Branch was a comparison analysis of the two aforementioned paints utilizing the original (PS7) and new (K2130) binders. Two samples per test would be simultaneously exposed to combined space environmental effects (CEE). One of these samples would have the PS7 binder and the other would have the K2130 binder.

This paper describes the CEE test facility used to requalify the white thermal control paint Z-93P and discusses the comparison analysis of Z-93 and Z-93P when simultaneously exposed to CEE. A post-exposure reflectance recovery phenomenon, bleaching, was observed and is discussed.

DESCRIPTION OF THE FACILITY

The Space Environmental Effects Branch at MSFC operates the CEE test system, which provides the unique capability to expose materials to a simultaneous or sequential simulated space radiation environment and perform in-vacuo reflectance measurements. The simulated space environment consists of protons, low-energy electrons, high-energy

electrons, vacuum ultraviolet (VUV), and near ultraviolet (NUV) radiation. The CEE test chamber is shown in Figure 1. This test system is composed of all Conflat™ metal seals and is maintained at a base pressure of 5×10^{-8} torr with four ion pumps. High-energy electrons and protons propagate through the vacuum from the National Electrostatics Corporation accelerators to the test chamber through two separate beam lines, each equipped with a beam profile monitor and Faraday cups. Each beam line Faraday cup is remotely moved into and out of the charged particle beam path.

The test chamber has a Faraday cup array, and each Faraday cup in the array is oriented to collect charge from a specific charged particle source (see Fig. 1). A temperature-controlled sample holder transports two 1-in diameter samples in the horizontal plane from the sample exposure position to the integrating sphere for in-vacuo reflectance measurement. The sample holder was maintained at 21 °C for this comparison test to reduce any sample heating effects.

During CEE exposure, the samples are rotated so the sample normal is +45° off the horizontal plane to allow them to be simultaneously exposed to all sources. High-energy electrons and protons impinge the sample surface at a 45° angle of incidence. The NUV irradiation also impinges at a 45° angle to the sample surface. The VUV and low-energy electrons impinge the sample at angles of 35° and 55°, respectively.

CONTAMINATION

A previous test, which subjected a trial Z-93 sample to a low dose of CEE, indicated the presence of a surface contaminant. That sample was prepared by AZ Technology. Figure 2 shows the detrimental effects of a photodeposited surface contaminant on Z-93. This Z-93 sample was exposed to a low dose of CEE's detailed in Table 1. After the exposure, an in-vacuo reflectance spectrum of the Z-93 sample was obtained. The CEE test chamber was repressurized with air to ambient pressure before the acquisition of the in-air reflectance spectra, also shown in Figure 2.

The Z-93 sample was placed in a standard sample holder and kept on a shelf in the laboratory. A reflectance spectrum was taken after 5,160 hr of ambient exposure. The data shown in Figure 2 indicate that the reflectance of this specific contaminant on Z-93 will not immediately recover when exposed to air, but low levels of surface contaminate on Z-93 will slowly recover reflectance with prolonged ambient exposure.

Supporting indicators, which showed that a contaminant was present, were rapid loss of VUV intensity and rapid reduction of electron flux from the electron flood gun. A visible contaminant layer was observed accumulating on the VUV source window; however, this layer was removed with solvent cleaning (methyl-ethyl ketone, acetone, and ethyl alcohol). The VUV intensity was reestablished after the contaminant layer was removed. The reduction of electron flux, from the electron flood gun, was not recoverable due to extensive contamination on the firing unit. The initial electron flux could not be restored even after extensive cleaning of the firing unit. The initial electron flux was eventually restored by removing the contaminated firing unit and installing a new electron flood gun firing unit. The contaminated firing unit was sent to the factory for refurbishment.

The CEE test system was cleaned, decontaminated, and verified to be contamination-free using techniques developed by the MSFC Space Environmental Effects Branch (ref. 2). Figure 3 shows the reflectance spectrum of the Z-93 sample utilized in the contamination-free verification test. This sample was exposed to 1,156.5 EHS of NUV and 50 KeV electrons at a fluence of 3.53×10^{15} electrons/cm². After the exposure, the test chamber was repressurized with air and a reflectance spectrum was obtained after 15 min in air. Figure 3 indicates the Z-93 sample experienced a reflectance recovery when air was used as a repressurant. This phenomenon is discussed below.

EXPOSURE SEQUENCE

Two white thermal control paint samples were obtained from IITRI: a Z-93 sample, number A-042 of batch R155 with the PS7 binder; and a Z-93P sample, number X-11 of batch S044 with the K2130 binder. The goal of this test was to expose these two samples to a 5-yr equivalent geosynchronous Earth orbit (GEO) dose of electron radiation. NUV and VUV exposure equivalent to 5 yr in GEO could not be performed without requiring extensive testing times. The NUV and VUV exposures were included to provide a testing environment approaching that of the natural space environment.

The simulated 5-yr GEO electron fluence was determined by calculating the dose-depth profile (obtained by using the Integrated Tiger Series 3 software (ref. 3)) for a 5-mil thick Z-93 sample. The dose-depth profile is shown in Figure 4.

The Z-93 and Z-93P samples were placed in the CEE test chamber and a pre-exposure in-vacuo reflectance measurement was taken when the vacuum level in the chamber reached 8×10^{-7} torr. The NUV and VUV exposures were initiated, after the pre-exposure measurement was obtained, with both sources providing nominally 2 UV Suns intensity on the samples. The VUV intensity was measured over the wavelength range from 120 to 200 nm. The NUV intensity was measured over the wavelength range from 250 to 400 nm. The samples were continuously exposed to NUV and VUV throughout the test, and the intensities were maintained at nominally 2 UV Suns. Sample exposure to 50- and 200- KeV electrons varied in duration from day to day; however, the beam current for each source was maintained at 1 nA/cm² during each electron exposure. In-vacuo reflectance measurements were obtained periodically throughout the duration of this test. The CEE exposure portion of the test was terminated after 3 wk of exposure, with a total dose of 953.5 ESH of NUV and VUV, 50 KeV electrons at a fluence of 1.2×10^{15} electrons/cm², 200-KeV electrons at a fluence of 7.35×10^{14} electrons. Figure 5 shows the reflectance of the two samples degraded similarly during this investigation.

REFLECTANCE RECOVERY INVESTIGATION

Previous data (Fig. 3) indicate that a reflectance recovery process will occur when Z-93 type paints are damaged with space environmental effects then repressurized with air. The term "bleaching" refers to those optical property recovery processes induced after introduction of gasses. A bleaching effect is a type of recovery process generally associated with exposure to air or some other gas containing oxygen. Figure 3 shows a bleaching effect after the Z-93 sample was irradiated and then repressurized with air as a fill gas. "Recovery process" refers to those processes that produce an increase in the reflectance of a material after the material experienced a decrease in reflectance due to space environmental exposure.

An attempt was made to back-fill the CEE test chamber with nitrogen, from liquid nitrogen boil-off, at a rate sufficient to monitor reflectance changes as a function of pressure. The nitrogen leak valve utilized lacked the required sensitivity for this procedure to be implemented, so the reflectance was measured as a function of time. The in-vacuo reflectance system was configured to monitor the sample reflectance at 600 nm, chosen because reflectance recovery is measurable at this wavelength (Fig. 3). The sample analyzed was Z-93P. Figure 6 shows that over a 10-min nitrogen back-fill time, the reflectance at 600-nm wavelength recovered by about 47 percent. After 10 min of nitrogen back-fill, the test chamber reached atmospheric pressure. Reflectance measurements of the Z-93 and Z-93P samples were obtained after a total of 113 hr in a dark closed nitrogen environment, with an interim measurement taken after 41 hr to determine if nitrogen produced any bleaching effects. Results indicate that extended exposure to a dark closed nitrogen environment produces little change in reflectance beyond the first 10 min of nitrogen exposure (Fig. 7)

After the reflectance spectra was obtained for the Z-93 and Z-93P samples, which remained in a dark closed nitrogen environment for 113 hr, the samples were removed from the CEE test system and measured, in air, by the laboratory portable spectrophotometer (LPSR). The transit time, in air, between the dark closed nitrogen environment of the CEE test chamber and the LPSR measurement was approximately 15 min. Results are also shown in Figure 7. After this measurement in air, the samples were placed in a standard sample holder and kept in a dark environment for 510 hr. Figure 7 shows that the samples experienced a slight recovery during the 510 hr in the dark ambient environment.

CONCLUSIONS

The IITRI-manufactured samples of Z-93 and Z-93P were exposed to equivalent doses of NUV, VUV, 50-KeV, and 200-KeV electrons. This test shows similar degradation in both samples when subjected to equivalent space environmental effects exposure. A conclusion is that Z-93P is a suitable replacement for Z-93.

During the course of this test, many observations were made concerning the response of Z-93 to a simulated space environment in addition to documenting the reflectance degradation of Z-93 and Z-93P in the simulated 5-yr GEO dose. Figure 2 shows that low levels of a surface contaminant photofixed on Z-93 does not experience rapid reflectance recovery when exposed to air. The reflectance of Z-93 with a low level surface contaminant will partially recover with prolonged exposure to air. Figures 5 and 7 show that the reflectance of Z-93, without a surface contaminant layer, will rapidly recover reflectance when exposed to air.

The nitrogen back-fill test was performed to determine if the bleaching effects, commonly observed when back-filled with air, could be eliminated or reduced and thus provide a guideline to measure sample reflectance ex-vacuo with some credibility. The results show that Z-93 samples experience a recovery in solar alpha of approximately 52 percent when back-filled and maintained in a dark closed nitrogen environment for 113 hr. It should be noted that this 52-percent recovery of solar alpha was observed after a specific CEE exposure was applied to the Z-93 sample. This specific dose was 953.5 ESH of NUV and VUV, 1.2×10^{15} electrons/cm² at 50 KeV, and 7.35×10^{14} electrons/cm² at 200 KeV. Another Z-93 sample was exposed to a CEE of 1,156.5 ESH of NUV and 3.53×10^{15} electrons/cm² at 50 KeV then repressurized with air. The solar alpha of this sample recovered by 71 percent after 15 min in air, as shown in Figures 3 and 7. Figure 8 summarizes the change of Z-93 and Z-93P solar alpha during this test. Solar alpha of both Z-93 and Z-93P increased with increasing CEE, and solar alpha recovered as the samples were exposed to nitrogen and, later, air. These results indicate that nitrogen repressurization can decrease the rate of reflectance recovery and, therefore, has a potential use in obtaining credible reflectance measurements ex-vacuo. The authors emphasize that this specific use of nitrogen, as a repressurant, requires further development.

REFERENCES

1. Babel, H.W. et al.: *Selection, Rationale, Application, Optical Properties and Life Verification of Z-93 for the Space Station*, August 1994.
2. NASA TM-108518, *Radiation Induced Degradation of the White Thermal Control Paints Z-93 and Z-93P*, October 1996.
3. *Integrated Tiger Series 3.0*, Oak Ridge National Laboratory, Radiation Shielding Information Center, CCC-467, 1994.

TABLE 1. Dose applied to the Z-93 sample shown in Fig. 2.

Source	Fluence
NUV	150 ESH at 2 UV Suns
VUV	150 ESH at 2 UV Suns
700 KeV protons	5×10^{13} protons/cm ²
200 KeV protons	6.3×10^{13} protons/cm ²
100 KeV protons	6.2×10^{13} protons/cm ²
200 KeV electrons	1.1×10^{14} electrons/cm ²
50 KeV electrons	1.9×10^{14} electrons/cm ²

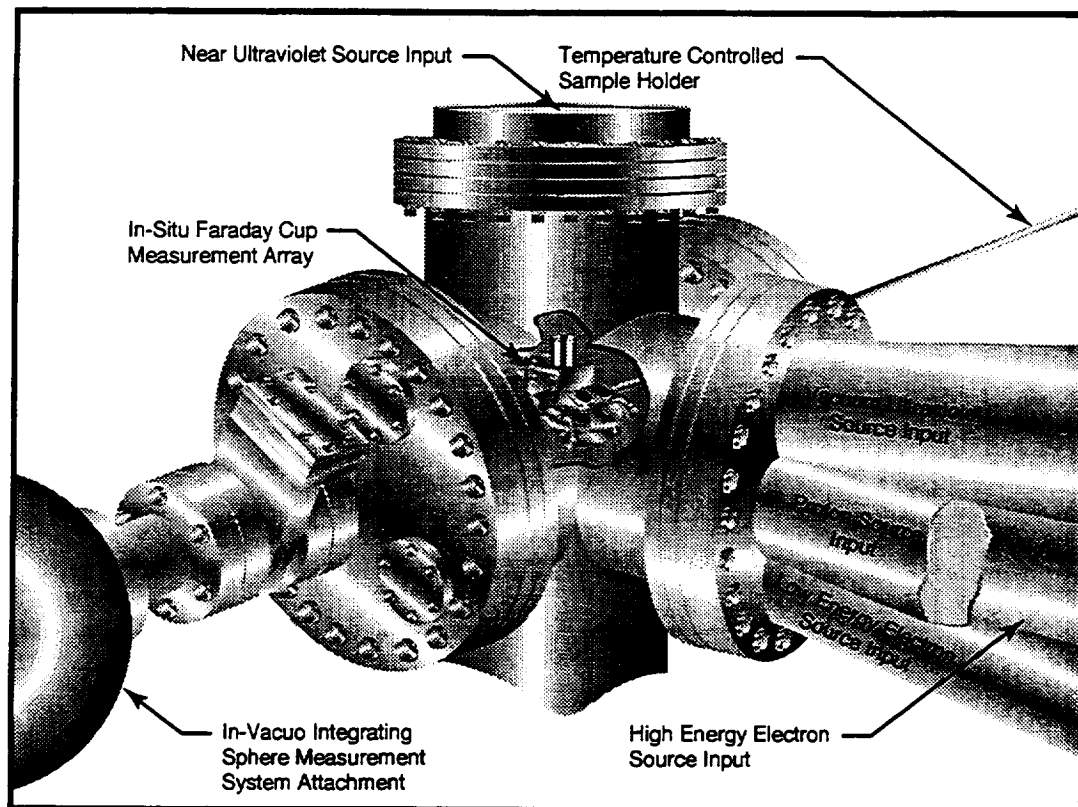


FIGURE 1. CEE test chamber

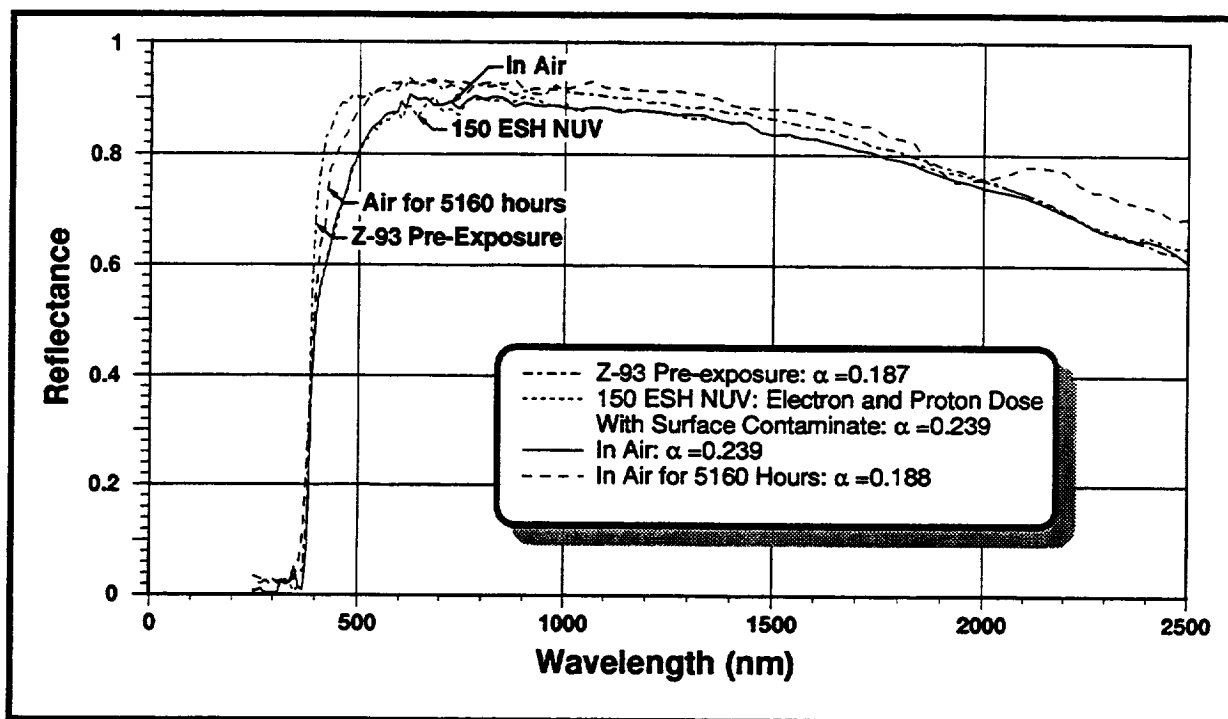


FIGURE 2. Reflectance spectra showing photodeposited surface contaminant on Z-93 accumulated during a low dose CEE exposure.

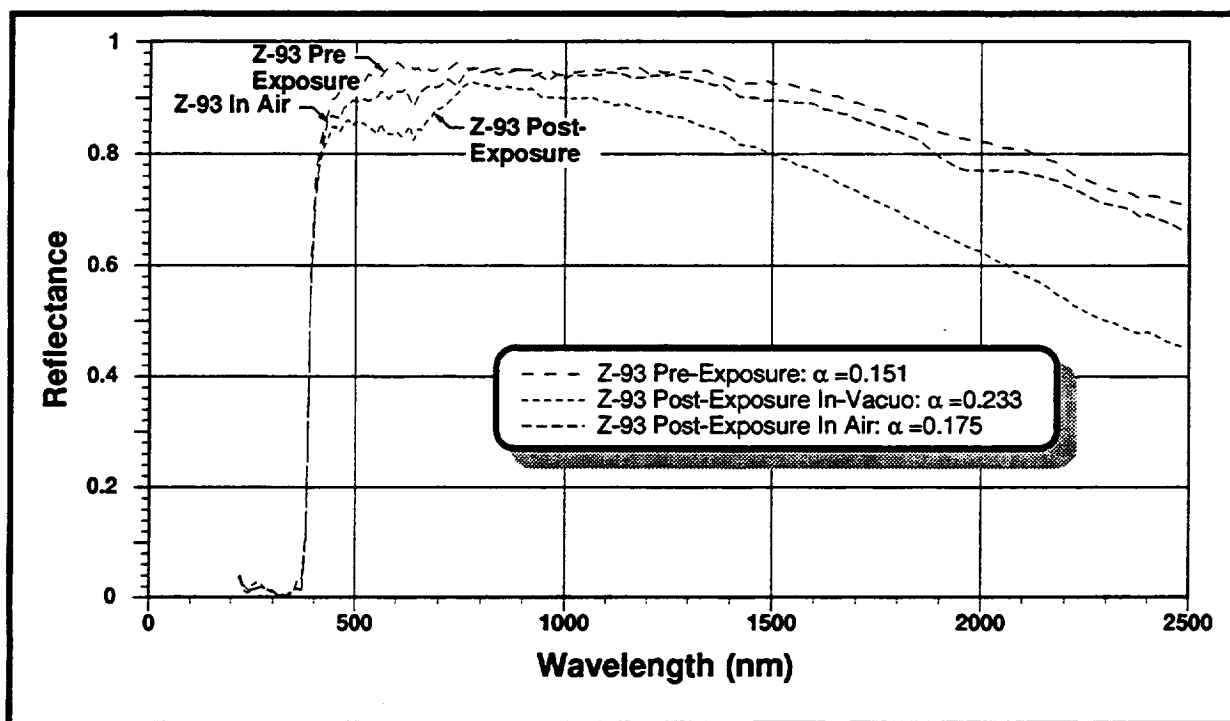


FIGURE 3. In-vacuo reflectance spectra of Z-93 exposed to CEE and repressurized with air.

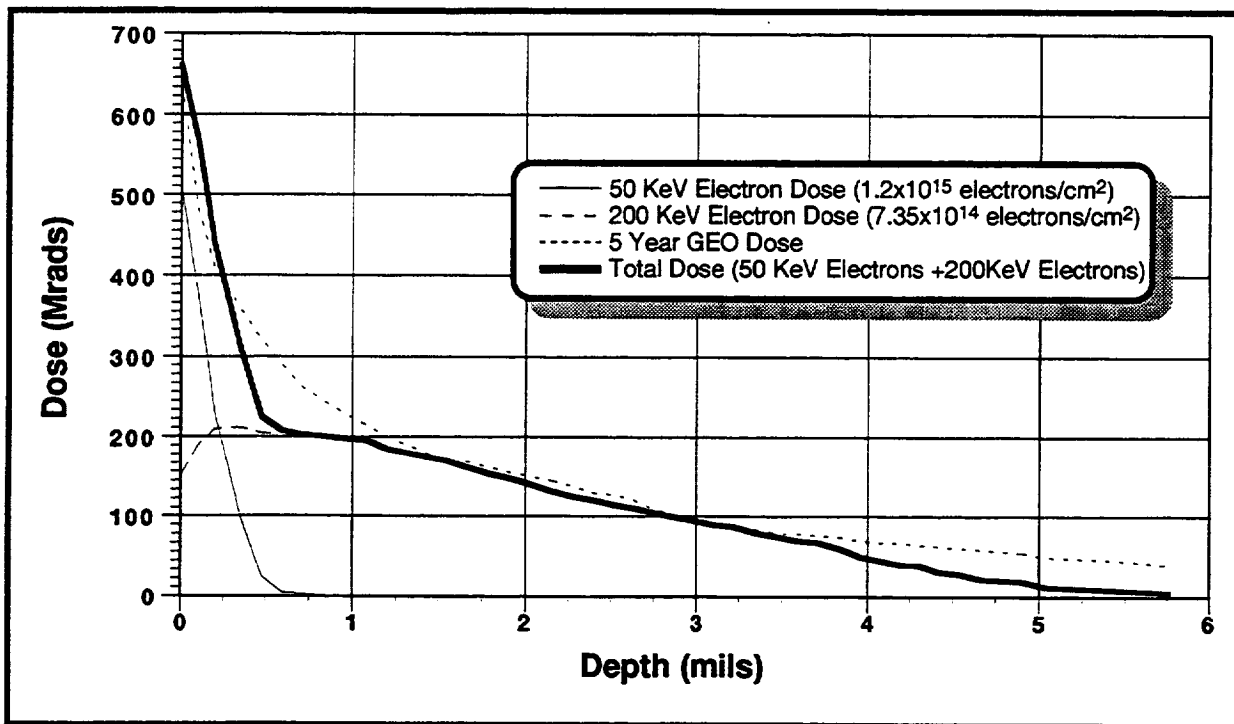


FIGURE 4. Dose-depth profile for Z-93 with a dose of to 50 KeV electrons at a fluence of 1.2×10^{15} electrons/cm², 200 KeV electrons at a fluence of 7.35×10^{14} electrons/cm² and a 5-yr GEO dose.

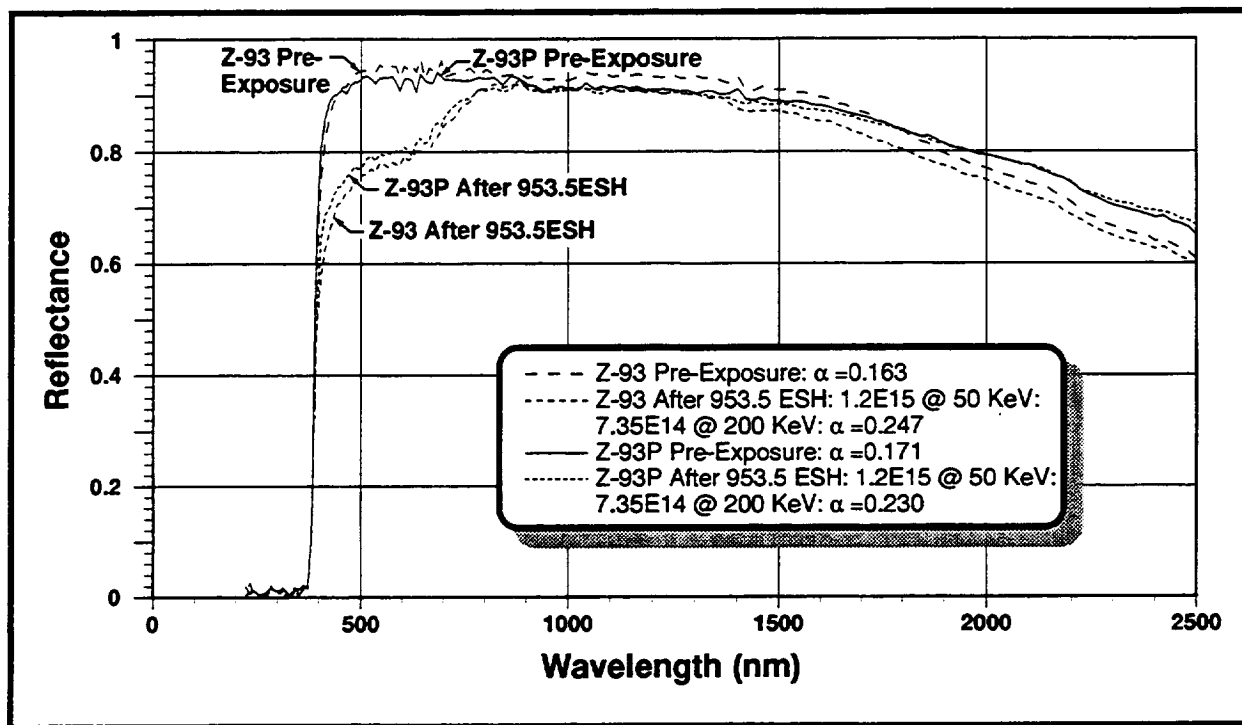


FIGURE 5. In-vacuo reflectance spectra of Z-93 and Z-93P after a cumulative dose of 953.5 ESH of NUV and VUV, 50-KeV electrons at a fluence of 1.2×10^{15} electrons/cm² and 200-KeV electrons at a fluence of 7.35×10^{14} electrons/cm².

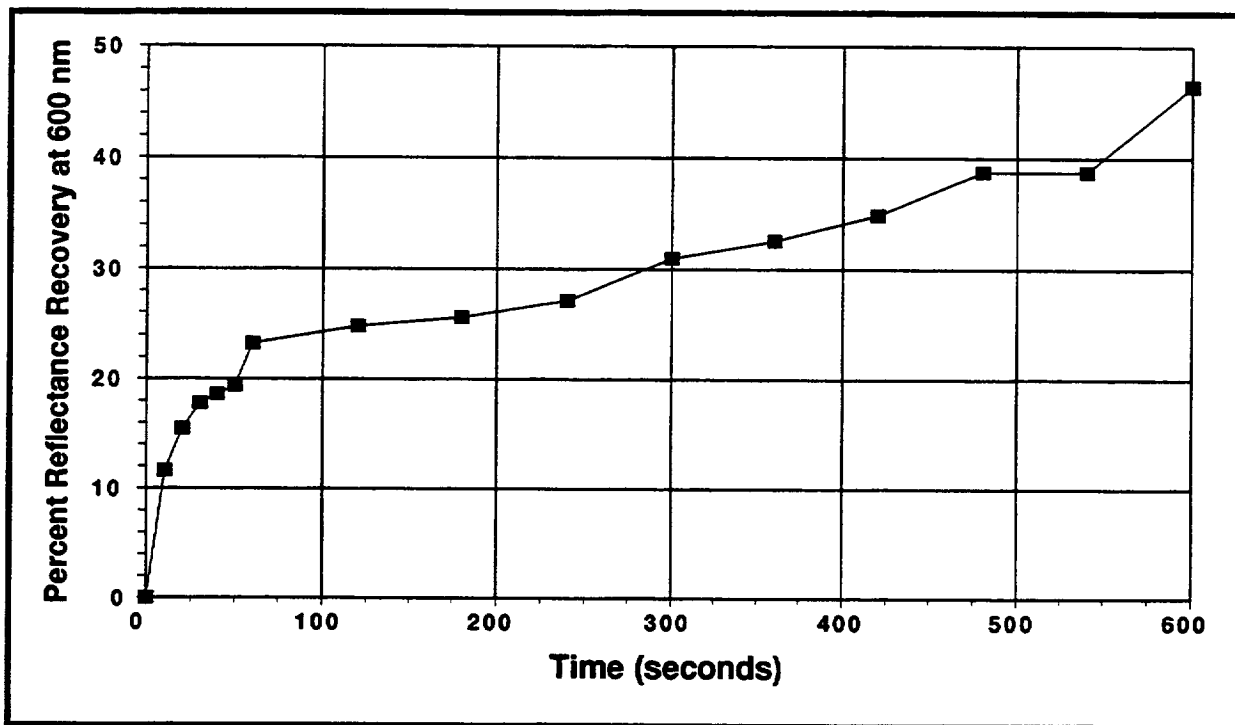


FIGURE 6. Data showing the percent reflectance recovery at 600 nm of the Z-93P sample during repressurization with nitrogen.

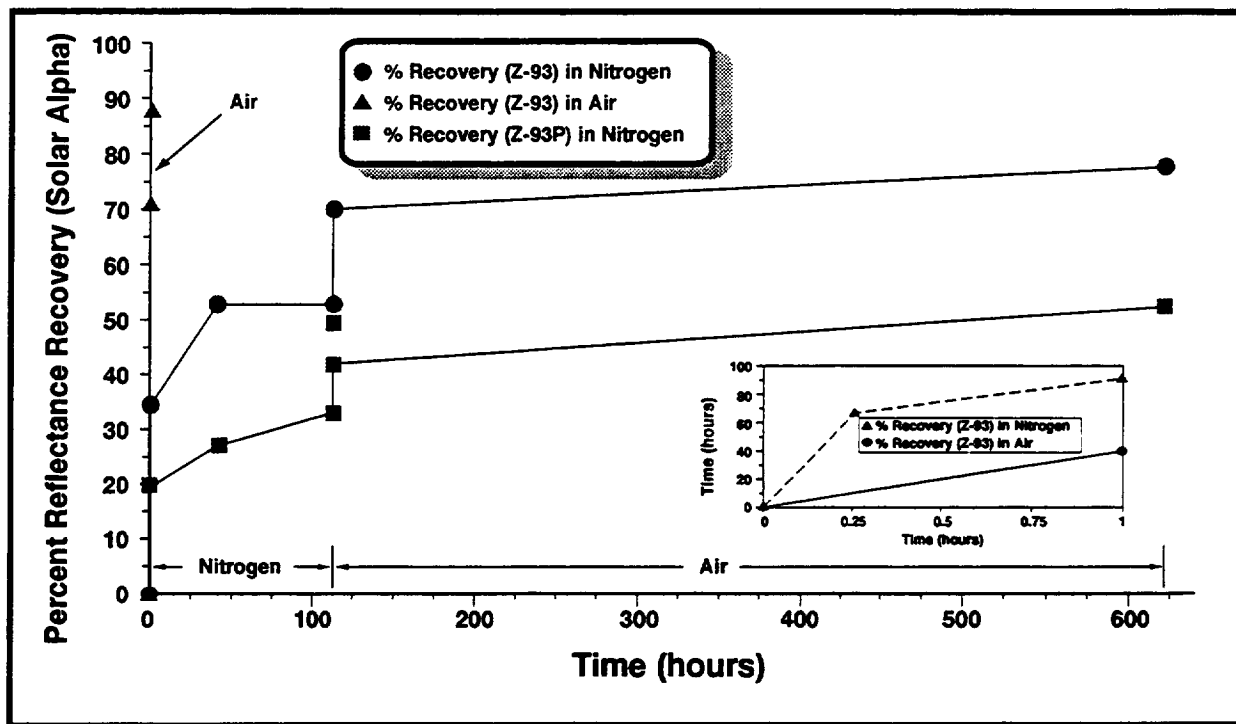


FIGURE 7. Reflectance of Z-93 and Z-93P after 1, 41, and 113 hr in a closed nitrogen environment then exposed to air for a total of 510 hr. This graph shows that the rate of reflectance of the Z-93 solar alpha was less when nitrogen was used as a repressurizing gas.

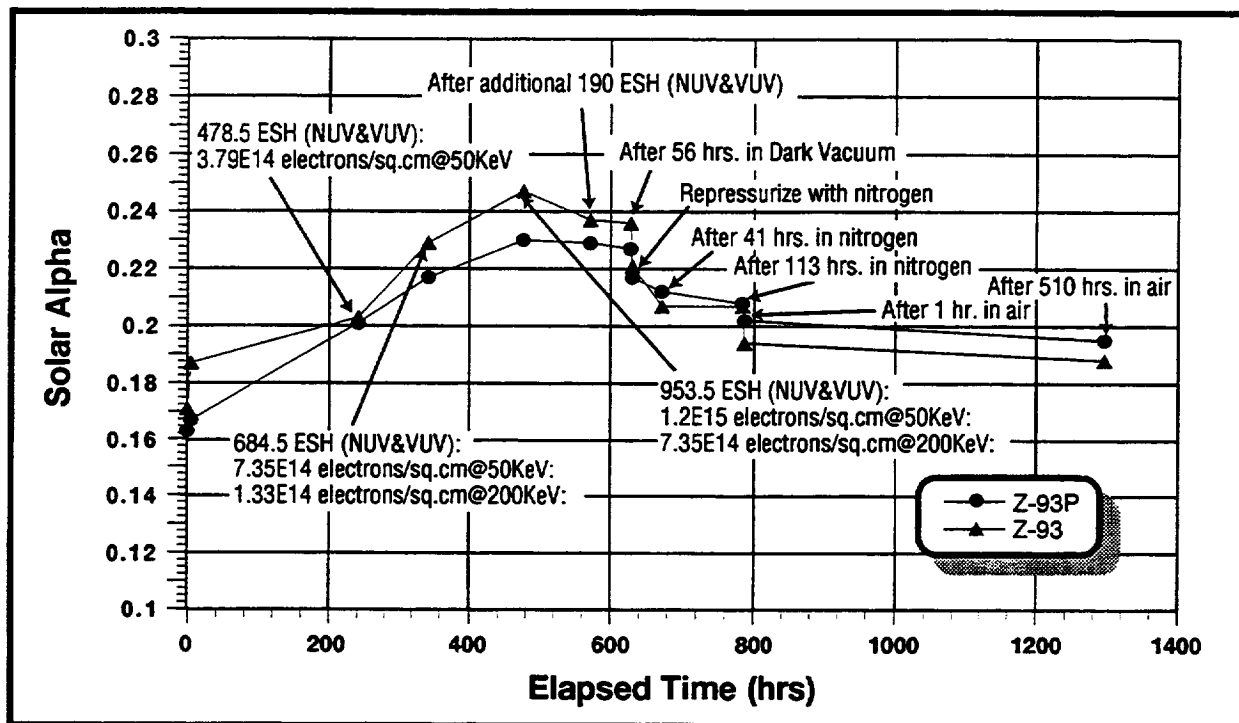


FIGURE 8. Summary of Z-93 and Z-93P solar alpha change during the CEE test.